Review Report on PhD Thesis

Faculty: **Central European Institute of Technology Brno University of Technology in Brno** Academic year: **2019/2020**

Student: **Jorge Alberto Torres Rodríguez**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **prof. Ing. Jozef Kaiser, Ph.D.**

Reviewer: **prof. RNDr. Jiří Pinkas, Ph.D.**

PhD thesis title: **Processing of aerogel coatings on bulk materials substrates**

Topicality of doctoral thesis:

The work of Mr. Torres Rodríguez, summarized in his doctoral thesis, is focused on the preparation by optimized synthetic routes of aerogels, xerogels, and powders of ZrO_2, YSZ, and lanthanide zirconates (LZ, $Ln_2Zr_2O_7$, Ln = La, Nd, Gd, and Dy) and on structural, morphological, thermal, and spectroscopic characterization of the obtained products. His studies are also directed at testing of four methods of aerogel coating fabrication. In a broader context, the work is aimed at the area of synthesis of materials suitable for thermal barrier coatings (TBCs) for the aerospace industry. This field at the borderline of inorganic, physical, and materials chemistry is currently a research area of vigorous activity and extreme importance.

Meeting the goals set:

The aims of the doctoral thesis are very briefly stated just on one page (p. 30) in an un-numbered paragraph, which is not even listed in the Contents. The goals are a systematic investigation of the synthesis and fabrication of thermally stable aerogels that would maintain the porosity and retain mechanical stability under harsh thermal conditions in high-temperature applications. For this purpose aerogels based on ZrO_2, YSZ, and four lanthanide zirconates (LZ, $Ln_2Zr_2O_7$, Ln = La, Nd, Gd, and Dy) were studied. The synthetic routes were optimized and several soft-chemistry coating methods tested. The resulting materials were characterized by suitable instrumental methods. Aerogel films were then examined under continuous heating-cooling cycles at the temperatures up to 1100 °C. The best $La_2Zr_2O_7$ aerogels featured enhanced thermal stability and retained its porous structure upon calcination. The deposition of a slurry of fine aerogel powder proved to be the best method to fabricate coatings that avoided shrinkage and detaching from the substrates. These results fulfill the goals of the dissertation.

Problem solving and dissertation results:

The major findings for the ZrO_2 and YSZ systems are that YSZ aerogel is more stable than ZrO_2 that suffers the complex m-t phase transition, which is dependent on the crystallite size and temperature (observed by TG/DSC and HTXRD). Due to the lack of phase changes, YSZ is less susceptible to dimensional changes upon calcination at 500 °C. However, porosity (N_2-adsorption, SEM) is completely lost in both systems at 1200 °C. Therefore four lanthanide zirconates ($Ln_2Zr_2O_7$, Ln = La, Nd, Gd, and Dy) were examined and prepared for the first time in aerogel form. They retain high surface areas at these calcination conditions. All these systems were prepared as powders, xerogels, and aerogels for the sake of comparison. Aerogel coatings were prepared by doctor blade, dip-coating in sol, and dip-coating in aerogel slurry procedures. The dip-coating in a slurry of 30% wt. of aerogel powder proved to be the most suitable approach leading to no shrinkage and detaching of the coating. $La_2Zr_2O_7$ aerogel coatings demonstrated enhanced thermal stability and retention of its porous structure upon calcination and even after continuous heating-cooling cycles.

Importance for practice or development of the discipline:

This dissertation work could evolve into an important practical processing procedure in the area of synthesis of materials suitable for thermal barrier coatings (TBCs) for the aerospace industry.

Formal adjustment of the thesis and language level:

The dissertation of Mr. Torres Rodríguez proves his ability to carry out independent research and obtain competitive results. The dissertation is based on two original papers published in Inorganic Chemistry (Q1 in Inorganic & Nuclear Chemistry) and The Journal of Supercritical Fluids (Q1 in Chemical Engineering) in 2019. In both papers, Mr. Torres Rodríguez is the first author.

The author should have paid better attention to punctuation, typing variables in italics, the English word order (SVOMPT), including one subject and one verb in a sentence, proper word selection, subject-verb agreement in number, correct use of preposition of, correct use of the phrase due to, selection of proper prepositions (under vacuum, not in vacuum), avoiding use of nouns as verbs (grow not growth), completing sentences, proper spelling (solid network instead of sold network). A list of grammatical and typing errors is listed as an Appendix to this thesis review for the candidate’s information and editing.

Questions and comments:

Comments listed below should be addressed in the preparation of the defense presentation but do not have to be explicitly discussed at the final defense:
Units of time should be h, not hrs.
p. 9 Abbreviations should be explained at their first occurrence (TBC).
p. 11 Table 2.1 – thermal conductivity data should be added.
p. 11 Are Figs. 2.2, 2.8, 2.9 original drawings, or should they be referenced?

p. 11 $M(OR)_4$ is not very general chemical formula, $M(OR)_x$ would be better. R is an organic residue, not parent alcohol.
p. 14 Steric impedance effects are usually called steric hindrance.
p. 21 Thick aerogel films (≈ 0.5 μm) versus p. 22 Thin aerogel films (≈ 25 μm)
p. 31 Table 3.1 Purity values listed for $Zr(OPr)_4$, NH_3, and HNO_3 are actually their concentrations, not purities. Hacac is acetyl acetone, acac is the abbreviation for acetyl acetonate anion. Why $ZrOCl_2 \cdot xH_2O$ is not listed among used reagents in Tab. 3.1?
p. 31, 32 Scheme 3.1 Ammonia is NH_3, NH_4OH does not exist.
p. 36 Source and properties of metallic substrates (Al, Ni) are not sufficiently described.
p. 39 Diffraction angles are usually presented in degrees of 2theta, not 65 °C.
p. 41 Viscosity was investigated in 3.2.2. What instrument was used?
p. 63 $La(NO_3)$ is missing the subscript 3.
p. 67 Table 4.8 is useless; all numbers are the same.
p. 69 There are no Zr-O bending vibrations – bending relates to an angle.
p. 76 …a weight loss of 15, 10.9, 13.1, and 9.4 %wt. There should be the same number significant figures.
p.76 …two maximums were observed ranging between 221-237 °C... It should be 212.
p. 79 Why there is no trace for CO2 in Fig. 4.24a?
p. 84 Two samples 125 and 250 microns were used, but Fig. 4.29 shows 150 microns?
p. 93 Fig. 4.36 – the lower trace should be 600 instead of 1000 °C.
p. 100 Ref. 24 – the publisher is missing.
p. 108 Ref. 108 The book of Sing is referenced as Buchbesprechung in Berichte. Should be cited appropriately.

Questions to be addressed during the final defense presentation:

1. What was the amount of water in 1M HNO_3 solution in PrOH? Was the amount of water coming from 70% HNO_3 counted in further calculations of stoichiometric ratios (p. 33)?

2. Yttrium(III) nitrate is hexahydrate, was this amount of water counted in further calculations of stoichiometric ratios (p. 34, 47)?

3. How do you know that the Ln^{3+} : Zr^{4+} molar ratio was constant at 1 : 1 (p. 34) when there is an unknown amount of water in $Dy(NO_3)_3 \cdot xH_2O$ (but molecular mass in Tab. 3.1 is used for hexahydrate, have you checked experimentally that x = 6 for $Dy(NO_3)_3 \cdot xH_2O$?) and $ZrOCl_2 \cdot xH_2O$ (not listed in Tab. 3.1 on p. 31)?

4. The molar ratio of $Zr(OPr)_4$, 1-PrOH, HNO_3, H_2O, and $Y(NO_3)_3$ is reported as 1 : 150 : 2 : 3 **: 0.14**. However, the YSZ aerogel is said to nominally consist of 7 mol% of yttrium (p. 34) while further on it is 7 mol% of Y_2O_3 (p. 47). Please explain.

5. What are the molar amounts of reagents ($Zr(OPr)_4$, HNO_3, H_2O) listed in Tab. 4.1, 4.2, 4.3 (p. 42, 43)? What are the yields of reported dried aerogels, powders, and xerogels?

6. Have any elemental analyses (e.g., ICP OES) been done for YSZ and $Ln_2Zr_2O_7$?

7. The pore size distribution of the samples was determined from the desorption isotherms using the Barrett-Joyner-Halenda (BJH). Have you compared the results with the DFT methods (p. 39)?

8. On p. 42 it is stated: At high concentrations of Acac, hydrolysis reactions are suppressed and condensation reactions are favored. How can condensation proceed without hydrolysis?

9. Are these really new pores exposed, as observed in Fig. 4.7b (p. 55) or are there just small NPs?

10. The crystallite size as a function of the lanthanide ion mass in Fig. 4.16d (p. 68) decreases for powder but increases for xero- and aerogels. However, the opposite trend is stated on p. 69:….
the trend is the higher the atomic number, the smaller the crystallites. What is the origin of this effect?

11. What is the origin of the sharp peaks in Fig. 4.23 (p. 76-77)? Exothermic evaporation of acetone after water does not seem plausible.

Conclusion:

This work as a whole is focused on very topical areas of inorganic materials, aerogel structures, and coating fabrication with large application potential. Synthetic experiments brought us a number of new results and some previously unknown facts were discovered. The author demonstrated his ability to carry out both synthetic experiments and a wide array of characterization measurements by structural, microscopic and spectroscopic techniques. Six oxidic systems were prepared and characterized by powder X-ray diffraction studies to their phase composition and phase transformations at elevated temperatures, by scanning electron microscopy for their morphology, nitrogen adsorption for surface area and porosity, and their chemical properties experimentally established. The author is capable of analyzing obtained data and drawing reasonable conclusions based on experimental facts. Figures, schemes, and graphs presented throughout the work are clearly rendered and convey information to a reader. A large number of references (153) and their temporal distribution shows that the author possesses a good comprehension of the past and current status of the field and its recent developments. The author should have paid better attention to English grammar, word selection, and sentence construction. Two papers based on the results obtained in this thesis were already published in international journals with Mr. Torres Rodríguez as the first author. This peer-reviewed publication demonstrates the candidate`s ability to obtain and communicate scientific results of a high standard. Furthermore, he is the co-author of other papers and conference presentations.

In conclusion, I can declare that the overall amount and quality of this work is adequate for a doctoral thesis. In my opinion, the reviewed thesis fulfills all requirements posed on theses aimed for obtaining a Ph.D. degree. This thesis is ready to be defended orally in front of the respective committee. I recommend this work to be accepted in partial fulfillment of requirements for a Ph. D. degree

In Brno, on February 16, 2020

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prof. RNDr. Jiří Pinkas, Ph.D.

Appendix

Comments on English grammar

metallic oxide = metal oxide
p. 22,24,25,26,27,29,51,62 ……, such as
p.15 due to these reactions continues
p.16 the sold network
p. 21 acoustic waves is substantially increased
p. 23,25,29… missing preposition of
p. 25 due to demonstrate low thermal conductivity, …..that render them for TBCs applications.
p. 26 Due to the exposed area is large,… due to any impurity decrease the gel adhesion
…and then withdrawal it from the sol.
p. 27 Exist a variant of the dip-coating method, which….Fenech et.al. [55] compared to the deposition of three YSZ, et.al.
p. 29 was developed a doctor-blade method to deposit………the effect of synthesis parameters… in the porosity, The final coatings were produced of 10 - 40 µm thick.
p. 35 all the wet gels intended to transforms into an aerogel
p. 37 the metallic substrate was drowned and withdrawal to produce, to avoid the sol turns to a wet gel
p. 38 monitoring of the mass changes of a sample in function of the temperature
p. 39 degassed in vacuum
p. 51 due to there is no significant mass loss
p. 55 processes are due temperature effect
p. 56 due to such change that can incur adverse results
p. 59 the ZrO_2 aerogel experiment a phase evolution upon heat treatment is as follows:59
p. 59 the crystals growth between 45-52 nm
p. 65 However, has been reported
p. 66 From these two experiments is reasonable the fact that
p. 67 From these experiments can be stated that, materials were summited to a heat treatment
p. 67 …structure consistent to the Miller indices, diffraction peaks … located at 2θ on 36° and 45°
p. 68 Fuentes et.al. obtained…
p. 72 However, was not possible to clearly state whether fluorite or pyrochlore structures.
p. 83 aerogels that after calcination process experimented high densification
p. 95 A simplified synthetic route allowed obtaining high-purity aerogel materials was found.
p. 97 However, the consolidation aggregate-aggregate and adhesion coating-substrate need to be enhanced due was not able to withstand the heating-cooling cycling test.